UNIVERSITI PUTRA MALAYSIA

EFFECT OF ALKALINE EARTH METAL (M= Sr, Ca and Mg) SUBSTITUTION ON DIELECTRIC PROPERTIES OF BaI-xMxPbO3 CERAMICS

ARI SULISTYO RINI

FSAS 2002 41

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By

ARI SULISTYO RINI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of Requirement for the Degree of Master of Science

August 2002

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Associate Professor Wan Mohd. Daud Wan Yusoff, Ph.D.

Faculty: Science and Environmental Studies

$BaPbO_3$-based ceramic have been the subject of numerous laboratory investigations, structurally and electrically. $BaPbO_3$ is a polycrystalline that possesses perovskite crystal structure, which is similar to the prototype dielectric ceramic i.e. $BaTiO_3$ structure. It is obviously noticed that suitable substitution on a system, enables us to change electrical properties of material to obtain specific requirement.

In this work, alkaline earth metals (i.e. Sr, Ca and Mg) were used as substitution elements. The substitution, which are based on ionic radii consideration ($r_{Mg} < r_{Ca} < r_{Sr}$), are attempted to drive the metallic properties of $BaPbO_3$ towards a semiconductor by creating either oxygen vacancies and/or allowing partial reduction of Pb^{4+} to Pb^{2+} there by stabilizing the unusual 3+ intermediate valency for Pb in the lattice. Dielectric studies of $Ba_{1-x}M_xPbO_3$ system (M = Mg, Sr and Ca) have not been reported so far.

The experimental investigation is divided into two categories. Firstly, x-ray diffraction methods and microstructural investigation, which is considered important in order to provide supportive evidence to any proposed model of dielectric behaviour. Secondly, the main experiment consists of alternating current conductivity measurement. Electrical tests on materials investigate their ability to store charge (capacitance) and transfer charge (conductance). Analyzing these parameters can provide valuable information in terms of a material's physical and chemical properties.

The results of XRD reveals lattice parameter changes of $BaPbO_3$ after substitution of Sr^{2+}, Ca^{2+} and Mg^{2+}. Structural transitions were only detected from orthorhombic perovskite to pseudo-cubic perovskite after substituted by 70 mol% of Mg at Ba-site. It is obviously noticed that to maintain molecule constancy of the chemical reaction of $Ba_{1-x}Mg_xPbO_{3-x}$ indicate oxygen deficiency on the product. From SEM Micrograph, it is clearly seen that, the samples prepared after calcined and sintered at 800 °C for 6 hours and 850 °C for 24 hours respectively, still contain high porosity.

The experimental results of deduced dielectric response from ac conductivity measurement were then separated into two regions, i.e. bulk response and grain boundary response, using equivalent electrical circuit model. Effect of porosity was detected from the grain boundary response at low frequency region that dominated by dc conduction or hopping charge carrier at all range of sample. The bulk response that represented by high frequency region indicated the less dispersion behaviour.

Substitution of Sr^{2+}, Ca^{2+} and Mg^{2+} into Ba-site of $BaPbO_3$ has increased the resistivity and the dielectric constant of pure $BaPbO_3$. Substitution of Ca^{2+} has apparently give major contribution to increase the dielectric constant of $BaPbO_3$ as high as $7x10^4$ when substituted by 60 mol% of Ca^{2+} at Ba-site of $BaPbO_3$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

KESAN PENDOPAN METAL ALKALI TANAH (M= Sr, Ca, dan Mg) TERHADAP CIRI-CIRI DIELEKTRIK SERAMIK $Ba_{1-x}M_xPbO_3$

Oleh

ARI SULISTYO RINI

Ogos 2002

Pengerusi: **Profesor Madya Wan Mohd. Daud Wan Yusoff, Ph.D.**

Fakulti: **Sains dan Pengajian Alam Sekitar**

Seramik berasaskan $BaPbO_3$ telah banyak dilakukan penyelidikan keatasnya secara struktur dan kemampuannya untuk menghantarkan arus elektrik. $BaPbO_3$ adalah sejenis poli-hablur yang mempunyai struktur hablur perovskite, dimana ia mempunyai persamaan dalam seramik dielektrik prototype, sebagai contohnya struktur $BaTiO_3$. Dapat dipahami bahawa pengganti yang sesuai dalam sistem memungkinkan kita untuk mengubah benda yang bermuatan elektrik; yang pada akhirnya mendapatkan sesuai dengan yang diharapkan.

Dalam kajian ini, unsur alkali tanah (seperti Sr, Ca, dan Mg) telah digunakan sebagai elemen gantian. Bahan penggantian berasaskan jejari ion ($r_{Mg}< r_{Ca}<r_{Sr}$) adalah untuk mengubah bahan pengalir kepada bahan semikonduktor. Setakat ini, kajian mengenai dielektrik pada sistem $Ba_{1-x}M_xPbO_3$ (M=Sr, Ca, dan Mg) masih belum dilaporkan.

Kajian penyelidikan telah dibahagikan ke dalam dua kategori. Yang pertama kaedah belauan sinar-x dan penyelidikan mikrostruktur dimana ia dianggap penting untuk membuktikan sifat dielektrik pada sebarang model cadangan. Keduanya, kajian utama untuk mengukur pengaliran arus. Ujian elektik ke atas bahan kajian adalah untuk mengetahui kemampuannya untuk menyimpan cas (kapasitans) dan memindahkan cas (konduktans). Penganalisaan parameter-parameter ini dapat memberikan maklumat pada sifat fizikal dan kimia bahan tersebut.

Keputusan XRD menunjukkan bahawa parameter kekisi $BaPbO_3$ berubah selepas digantikan oleh Sr^{2+}, Ca^{2+}, dan Mg^{2+}. Struktur transisi hanya dapat dikesan dari orthorhombik perovskite kepada pseudo-kubus perovskite selepas digantikan dengan 70 mol% Mg pada tapak Ba. Adalah jelas bahawa untuk mengekalkan konsistensi molekul pada tindakbalas kimia $BaPbO_3$ dicirikan dengan kekurangan oksigen pada produk. Daripada mikrograf SEM, dapat dilihat sampel yang disediakan selepas pengkalsinan pada 800°C selama 6 jam dan persinteran 850°C selama 24 jam, masih mempunyai keadaan berongga yang tinggi.

Dari keputusan eksperimen, sambutan dielektrik yang dideduksikan daripada pengukuran pengaliran arus ulang-alik, kemudian dibahagikan kepada dua bahagian, iaitu sambutan pukal dan sambutan sempadan butiran menggunakan model litar elektrik yang sepadan. Kesan keronggaan telah dikesan dari sambutan sepadan butiran bahagian frekuensi rendah yang didominasi oleh pengaliran arus terus atau pembawa cas loncatan pada pelbagai jenis sampel. Sambutan pukal yang diwakili oleh bahagian frekuensi tinggi dicirikan dengan sifat pengukuran penyebaran.

Penggantian Sr, Ca, Mg ke dalam tapak Ba pada $BaPbO_3$ telah meningkatkan ketahanan dan pemalar dielektrik $BaPbO_3$ sehingga $7 x 10^4$ apabila digantikan dengan 60 mol% Ca^{2+} pada tapak Ba.

ACKNOWLEDGEMENTS

I would like to express my great appreciation and sincere gratitude to Associate Professor Dr. Wan Mohd. Daud Wan Yusoff and Professor Dr. Abdul Halim Shaari for their sponsoring and supervision, exactly their help made my dream of pursuing higher education come true. I am indebted to my co-supervisor Dr. Zainul Abidin Hassan and Associate Professor Dr. Anuar Kassim, for his patience and valuable guidance and advise throughout this study.

I would like to thank to Mrs. Iftetan, Miss Huda Abdullah and all my lab-mates for their tremendous assistance and encouragement during the whole study period.

My appreciation goes to my closest friend Daryani and Gamma for the amity, patience and encouragement and to all my country-mates Harini Boekhari, Lailan Saufina, Mayastri, Penni Ismiati and Rini Yanti for the kindly cares, helps and their religious guidance and to all my college-mates Ernawati, Neila, Mirna, Sifa, Tesa, Ayu and Maesaroh who always be beside me whenever I needed them.

Finally, but not least, I most greatly appreciate my Mother, my brothers and sister, my aunt, my uncle and my cousins, for their support and encouragement.

I certify that an Examination Committee met on 29th August 2002 to conduct the final examination of Ari Sulistyo Rini on her Master of Science thesis entitled "Effect of Alkaline Earth Metal Substitution (M= Sr, Ca and Mg) on Dielectric Properties of $Ba_{1-x}M_xPbO_3$ Ceramics" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

ZAINAL ABIDIN TALIB, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

WAN MOHD. DAUD WAN YUSOFF, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ABDUL HALIM SHAARI, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ZAINUL ABIDIN HASSAN, Ph.D.
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ANUAR KASSIM, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

SHAMSHER MOHAMAD RAMADILI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 30 SEP 2002

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the supervisory committee are as follows:

WAN MOHD. DAUD WAN YUSOFF, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

ABDUL HALIM SHAARI, Ph.D.
Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ZAINUL ABIDIN HASSAN, Ph.D.
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ANUAR KASSIM, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ARI SULISTYO RINI

Date: 14 Sept 2002

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α	spectral parameter
ε	dielectric permittivity (F/m)
ε_{inf}	dielectric permittivity at very high frequency
ε_r	relative dielectric permittivity
$\varepsilon^*(\omega)$	complex permittivity as a function of angular frequency
$\varepsilon'(\omega)$	the real part of complex permittivity as a function of angular frequency
$\varepsilon''(\omega)$	the imaginary part of complex permittivity as a function of angular frequency
$\chi^*(\omega)$	complex dielectric susceptibility
χ'	real part of dielectric susceptibility
χ''	imaginary part of dielectric susceptibility
λ	wave length
μ	micron
ρ	resistivity (ohm/cm)
σ	conductivity (mho/cm)
$\sigma(\omega)$	conductivity as a function of angular frequency
τ	relaxation time (sec)
ω	angular frequency
ω_p	peak angular frequency
ω_c	critical angular frequency
$\propto$	proportional to

Å	Angstrom unit
a, b, c	lattice parameters
eV	electron volt
exp	exponential
f	frequency
h, k, l	Miller indices
j	$= \sqrt{-1}$
k	Boltzmann constant
kHz	kilohertz
ln	natural logarithm
log	logarithm
mHz	millihertz
Ac	alternating current
B	susceptance (mho)
C	capacitance
C'	real part of capacitance
C"	imaginary part of capacitance
DC	direct current
E	activation energy
FRA	Frequency Response Analyzer
G	Conductance
HP	Hewlett Packard
Hz	Hertz
I	current
Im	imaginary part

K	Kelvin
MHz	megahertz
R	resistance (ohm)
Re	real part
R_s	series resistant
SEM	scanning electron microscopy
T	absolute temperature (Kelvin)
UPM	Universiti Putra Malaysia
UM	Universiti Malaya
V	voltage
XRD	x-ray diffraction
Y	admittance
Y'	real part of admittance
Y''	imaginary part of admittance
Y*	complex admittance
Z	impedance
Z'	real part of impedance
Z''	imaginary part of impedance
Z*	complex impedance

CHAPTER 1

INTRODUCTION

Evolution of electronic component and demands for advanced materials yield intensive investigations on electrical and structural properties of materials. Characterization and identification of physical phenomena of materials become more interesting as new theories emerge to explain the observed experimental phenomena.

Among the phenomena that are, being intensely characterized is the electrical behaviour. The electrical tests on materials reveal their ability to store (capacitance) and transfer charge (conductance). Analyzing these phenomena can provide valuable information in terms of a material's physical and chemical properties including: impedance, porosity, tan delta, molecular relaxation, grain boundaries, phase changes, permittivity and modulus, along with many other parameters.

$BaPbO_3$-based ceramic have been the subject of numerous structural and electrical investigations. $BaPbO_3$ is a polycrystalline that possesses perovskite crystal structure, which is similar to the prototype dielectric ceramic i.e. $BaTiO_3$ structure. The discovery of superconductivity of Ba-Pb-Bi-O system has led to wide range of research on $BaPbO_3$-based system, included $BaPbO_3$ itself, though report of superconductivity below ~0.4 K in $BaPbO_3$ has not been confirmed by more recent studies (Mattheis 1990).

$BaPbO_3$ shows a metallic behaviour although there is no transition-metal ion present, and its resistivity has a small temperature dependent part. It is obviously noticed that suitable substitution on a system, enables us to change electrical properties of material to obtain specific requirement. For example, after Bi was doped into the Pb sites, superconductivity occurred at about 13 K along with a metal-insulator transition, which coincided with structural changes, whereas when Sb was introduced into Pb sites, no MI transition was found (Zhao 2000).

Alkaline earth metals (i.e. Ba, Mg, Sr, and Ca) were widely used as substitution elements. In some cases, they have been found to improve the electrical properties of Ba-based and Pb-based system to a specific requirement. Literature review on Mg, Sr, and Ca doped on Ba-site of $BaPbO_3$ were still sparse. What available is only limited to high-temperature thermoelectric properties of Ba-Sr-Pb-O and Positive Temperature Coefficient of Resistivity of Ba-Sr-Pb-O. Dielectric studies of $Ba_{1-x}M_xPbO_3$ system (M = Mg, Sr and Ca) have not been reported so far.

The substitution, which are based on ionic radii consideration ($r_{Mg} < r_{Ca} < r_{Sr}$), is an attempt to drive the metallic properties of $BaPbO_3$ towards a semiconductor by creating either oxygen vacancies and/or allowing partial reduction of Pb^{4+} to Pb^{2+} there by stabilizing the unusual 3+ intermediate valency for Pb in the lattice (Kodenkandath 2000).

Dielectric Analysis

Impedance Analysis is a powerful non-destructive tool for analyzing a range of electroceramic materials. The advantage of this technique is that it yields accurate and repeatable results, which are unobtainable by other electrical means. The properties of ceramic materials depend on close control of their structure in terms of